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THERMO-ELECTRIC ACTION WITH DUAL CONDUCTION OF ELECTRICITY

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In a paper¹ presented before the National Academy of Sciences in November, 1917, I discussed thermo-electric action in metals on the hypothesis of progressive motion by the 'free' electrons only. I have now extended the discussion to the case of dual electric conduction; that is, conduction maintained in part by the free electrons (electrons F) and in part by the associated electrons (electrons A), the latter passing directly from atomic union to atomic union.

I do this because, though we may not at present have a satisfactory theory² of electric conduction involving such action of the associated electrons, we are equally far from having a satisfactory theory of conduction as a function of the free electrons only.

I take it as self-evident that, whereas electric potential-gradient acts upon both free and associated electrons, tending to carry them in the direction of decreasing negative potential, free-electron pressure-gradient acts on the free electrons only. The necessary result of this consideration is the conclusion that, if electrons (A) as well as electrons (F) can move progressively through a metal, we shall, in a detached bar of metal having a temperature gradient from one end to the other, have a constant procession of free electrons from the place of high electron-gas pressure, the hot end of the bar, toward the place of low pressure, the cold end, while an equal procession of associated electrons moves in the opposite direction. For the mechanical tendency of the free electrons toward the cold end maintains an excess of negative potential at this end, with a corresponding deficiency at the hot end; and the electric potential-gradient thus established drives associated electrons from cold to hot, while it opposes, without being able entirely to prevent, the movement of free electrons from hot to cold.

The state of mobile electrical equilibrium thus presented to our imagination involves no violation of commonly accepted principles. The slight, extremely slight, reduction of electron mechanical pressure below the normal equilibrium pressure at the hot end of the bar induces there continual passage of the electrons from the associated to the free state, evaporation, let us say, with absorption of heat. At the cold end, on the other hand, the very slight excess of electrical mechanical pressure, above the normal value proper to the temperature, induces continual passage of electrons from the free to the associated state, condensation, let us say, with release of heat. The whole operation carries heat from the hot to the cold end of the bar, and it is, in fact,

somewhat analogous to the action of a steam heating-system, the free-electron movement corresponding to the stream of steam and the associated electrons movement to the return flow of the water.

My conception of the action, for a case in which there is no lateral loss or gain of heat, is set forth diagrammatically in figure 1, in which the dotted lines indicate movement of the free electrons and the full lines movement of the associated electrons.³

In my previous paper,¹ dealing with the hypothesis of progressive motion of 'free' electrons only, I rejected as unnecessary the assumption of a specific attraction of metals for electrons. But with the more complicated conditions dealt with in the present paper we cannot avoid this assumption; for without it we should have thermal conduction without initial difference of temperature, and so a violation of the second law of thermodynamics, in a bar of alloy varying in composition from metal α at one end to metal β at the other. There must be no progressive movement of free electrons from one end to the other, or of associated electrons in the opposite direction, in such a bar. The superior mechanical pressure of the free electrons at the α end will produce a slight initial movement establishing a potential gradient along

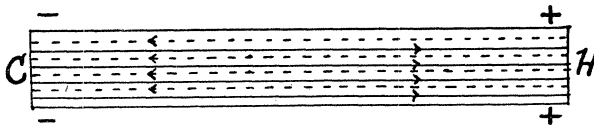


FIG. 1

the bar, the α end becoming positive and the β end negative; but the influence of this potential gradient on the associated electrons must be offset by a specific atomic attraction directed toward the β end. It is reasonable to suppose that the smaller free-electron density at the β end is due to the superior attraction of the β positive nucleus compared with the α nucleus. The resulting equilibrium, the inhibition of circulation of the electrons from one end to the other of the bar and back, is analogous to the equilibrium in a system made up of water, water-vapor, and a solution-column sustained by osmotic pressure. The upper end of such a column, with its reduced vapor-pressure, corresponds to the β end of our bar with its small free-electron pressure. The force of gravitation, directed from the top to the bottom of the column, is analogous to the electrical potential gradient from the β end toward the α end of the bar.

Naturally the question arises whether a bar of one metal having a temperature gradient, and a free electron density rising with the temperature, has not a differential specific attraction tending to move electrons toward the cold end. There may be such an attraction, and it will be well for us to take account of it, but where there is a temperature-gradient we are not

obliged to suppose a dead-lock between the potential gradient and this differential specific attraction. The conception of electron circulation, with thermal conduction (or convection), in a detached unequally heated bar survives the admission of specific attraction; but the whole matter now becomes more involved.

In addition to the potential, P , due to electric charge, we must now think of a potential, P_a , due to the differential attraction of the unequally heated, unhomogeneous, metal for the associated electrons, and also of a potential, P_f , due to the differential attraction of the metal for the free electrons. Both classes of molecules are subject to the charge-potential P , but electrons (A) only are subject to the potential P_a , and electrons (F) only are subject to the potential P_f .

Under hypothesis (A): If we assume, as hypothesis (A), that the mechanical tendency of the free electrons, if acting without electric forces, would produce equality of pressure from end to end of the bar, the condition of equilibrium (see fig. 1) in a detached bar hot at one and cold at the other is

$$\mu \left[\left(\frac{dl}{dl} \cdot dl + \frac{d(P + P_b)}{dl} \cdot nedl \right) \div nmdl \right] ne = -k_a \frac{d(P + P_a)}{dl} \quad (1)$$

where (dp/dl) is the gradient of mechanical pressure of the free electrons along the bar of length l , n is the number-density of the free electrons in the metal, m is the mass and e the charge of an electron, μ is the coefficient of mobility of the free electrons through the metal, and k_a is the electric conductivity of the metal, so far as conductivity is due to the electrons (A).

A simple formula,

$$\mu = k_f \cdot \frac{1}{Gme^2}, \quad (2)$$

where G is $(1/m)$, connects μ with the free-electron specific conductivity, k_f . Evidently

$$G = nv, \quad (3)$$

where v is the volume of one gram of free electrons in the metal.

Very simple operations, using equations (2) and (3), derive from (1) the form

$$(P_c - P_h) + \int_h^c \frac{k_f}{k_a + k_f} \cdot dP_f + \int_h^c \frac{k_a}{k_a + k_f} \cdot dP_a = \frac{1}{Ge} \int_c^h \frac{k_f}{k_a + k_f} \cdot v dp, \quad (4)$$

in which the integration extends from the hot end (h) to the cold end (c) of the bar.

The first member of this equation is the amount of reversible work that would be done by or on the unit quantity of electricity in passing *through* the bar, if it were made part of a closed thermo-electric circuit. This is something different from, probably smaller than, $(P_c - P_h)$, which is the *charge* poten-

tial-difference between the two ends of the bar. The quantity expressed by the whole first member I shall call the *virtual* e.m.f., resident in the bar because of its temperature gradient.

The form of the second member shows that the virtual e.m.f. can be represented by an area on the P - V plane. Thus, if the line AD in figure 2 represents the pressure-volume relations of the free electrons for the whole length of the bar, so that

$$\text{area } EADG = \int_c^h v dp,$$

we shall have

$$\text{area } EA'D'G = \int_c^h \frac{k_f}{k_a + k_f} \cdot v dp,$$

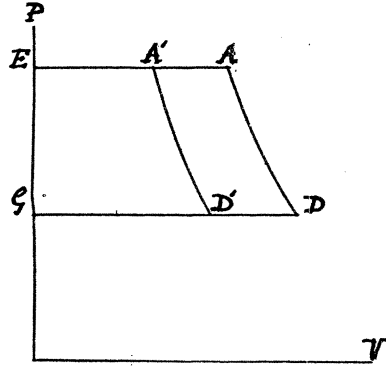


FIG. 2

provided we make the width of this area correspond at every height to the value of $k_f/(k_a + k_f)$ for that height.

Without the conception of dual conductivity and specific attraction we should, as my previous paper¹ shows, have in place of (4) the simple equation

$$P_c - P_h = \frac{1}{Ge} \int_c^h v dp.$$

with dual conductivity but without specific attraction we should have

$$P_c - P_h = \frac{1}{Ge} \int_c^h \frac{k_f}{k_a + k_f} \cdot v dp.$$

Obviously, then, the participation of the electrons (A) in the conductivity reduces the e.m.f. due to the temperature gradient in the bar. In fact, the part which associated electrons play in thermo-electric action is analogous to that played by entrained water in the work done by steam. The larger the

proportion of water, the smaller is the mechanical effect per unit mass of the mixture.

In the isothermal alloy 'bridge,' of composition varying from pure α at one end to pure β at the other end, which is supposed to connect the two metals at their hot or at their cold ends, we must have, when it stands detached, no cyclic movement of the electrons. Accordingly we get, in place of equation (1), the two equations

$$dP + dP_a = 0 \quad (5)$$

and

$$dP + dP_f = -\frac{dp}{ne} = -\frac{1}{Ge} \cdot v dp. \quad (6)$$

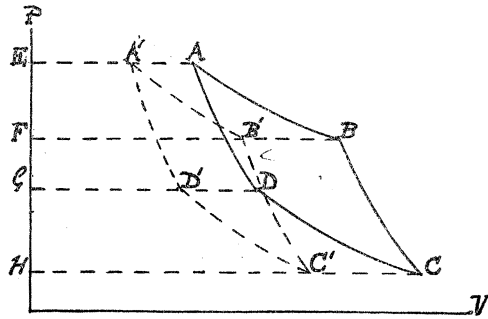


FIG. 3

These lead to the following, as the expression for the *virtual* e.m.f. due to the non-homogeneity of the isothermal bridge:

$$\int_{\alpha}^{\beta} \frac{k_f}{k_a + k_f} (dP + dP_f) = \frac{1}{Ge} \int_{\beta}^{\alpha} \frac{k_f}{k_a + k_f} \cdot v dp. \quad (7)$$

The first member of (7) is the reversible work that would be done, on the free electrons only, during the passage of the unit quantity of electricity through the bridge.

The expression for the work done on the electrons (A) is absent here, for the reason that, according to equation (5), no *reversible* work would be done on them.

For a thermo-electric circuit, made up of a bar of metal α , a bar of metal β , and two isothermal alloy bridges α - β , we find the net, or total, virtual e.m.f. to be represented by $(1 \div Ge)$ times the area $A' B' C' D'$ in figure 3, where $A B$, $B C$, $A D$, and $D C$ indicate the pressure-volume relations of one gram of free electrons in the four parts of the circuit respectively, and $A' B'$, $B' C'$, $A' D'$, $D' C'$, are found respectively from the corresponding full lines by means of the ratio $k_f \div (k_a + k_f)$, applied as in figure 2.

In spite of the conspicuous part which the specific potentials P_a and P_f

play in the local virtual e.m.fs. of the circuit, we can, by making a gap in any isothermal homogeneous part of this circuit and inserting there an electrometer, measure the total e.m.f. as a simple difference of charge-potential. The total, or net, amount of work done by or against the specific attractions which enter into P_a and P_f is zero for any quantity of electricity which goes completely through the circuit.

Under hypothesis (B): If, in place of hypothesis (A), we assume that the mechanical tendency of the free electrons is towards the condition of equilibrium which holds for thermal effusion, each local virtual e.m.f. will be represented by an area like $E' A' D' G' g'e'$ in figure 4, where E' is the mid-point of $E A'$ and G' is the mid-point of $G D'$. But the combination of four such areas, one for each of the lines $A' B'$, $B' C'$, $A' D'$, and $D' C'$, of figure 3, will give precisely the same net result that is represented in figure 3 by

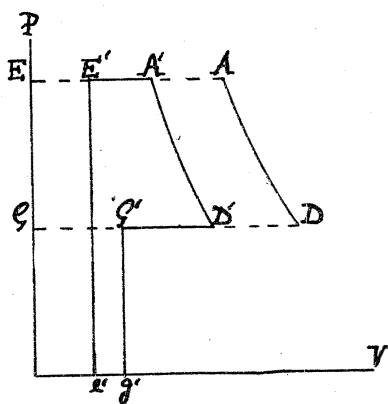


FIG. 4

$A' B' C' D'$. The total e.m.f. is, then, precisely the same under hypothesis (B) as under hypothesis (A). This is because the fundamental conditions of p and v , represented by the lines $A B$, $B C$, $C D$, and $D A$, in figure 3, remain substantially the same under hypothesis (B) as under hypothesis (A).

¹ These PROCEEDINGS, 4, 1918, (29-35).

² For suggestions see a paper by myself in these PROCEEDINGS, March, 1917, and one by P. W. Bridgman in the *Physical Review*, April, 1917, p. 269.

³ I am not without hope that the mechanism here suggested will prove to be of great service in the theory of heat conduction. It seems probable that the free electrons within a metal are quite incapable, acting as a permanent gas, of accounting for the magnitude of the metal's heat conductivity. But it is a familiar fact that the heat-carrying power of a vapor, involving evaporation and condensation, is vastly greater than that of a permanent gas. It appears, from the imperfect data now at my command, that the operation illustrated by figure 1 would give thermal conductivity of the right order of magnitude.

This conception of thermal conductivity, a conception occurring quite incidentally and unexpectedly, has already been communicated to the American Physical Society in a paper read at the meeting of December, 1917.